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## **Methodology for Evaluating Pesticides for Surface Water Protection II: Refined Modeling**

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### **1. Introduction**

The Surface Water Protection Program (SWPP) is developing a more consistent and transparent method for evaluating registration packages. The overall introduction for the evaluation procedure has been presented in Part I of the two-part reports. In summary, a two-phase procedure was proposed for surface water quality protection in assessing pesticides submitted for registration in California. Phase I evaluation is conducted to classify pesticides as to whether they are unlikely to be a surface water quality problem, or may potentially cause problems and require additional evaluation. For the latter case, phase II evaluation is performed to predict pesticide exposure and risk at the edge of fields based on refined modeling approach. The evaluation results are summarized as registration recommendations, i.e., [1] to support registration without conditions for pesticides which are unlikely to be a surface water quality problem, [2] to support conditional registration with requests for analytical methods for pesticides which may potentially cause surface water problems, or [3] not to support registration for pesticides which pose unacceptable potential surface water impacts.

In the proposed evaluation procedure, analytical methods will be required for pesticides with recommendation of conditional registration. In previous evaluations conducted by SWPP, conditional registrations are usually associated with requests for runoff test and/or sediment toxicity test. Those requests may not be appropriate for future pesticide registration process and post-use monitoring. First, model-predicted concentrations have been submitted for the requests of runoff test for some pesticides. It also suggested that estimated environmental concentration (EEC) by environmental fate models could be helpful in the pesticide registration process. In addition, sediment toxicity tests have been requested by USEPA for all pesticides with KOC > 1000 in the data requirement for pesticide registration (USEPA, 2007a). Therefore, sediment toxicity data is supposed to be available in the future for pesticide evaluation of new ingredients.

In addition to registration recommendations, the developed methodology also generates a *watch-list* of pesticide active ingredients for future evaluations by SWPP. The authorization of the watch-list is based on the California Food and Agricultural Code 12824 for “the continuous evaluation of all pesticides actually registered”. The watch-list will cover active ingredients for which registration is supported but potential exposure to surface water is identified. Potential actions for the listed active ingredients include: requesting analytical method for post-use monitoring, flagging the active ingredient for re-evaluation if its new label is associated with high-exposure use pattern, and other appropriate actions which may be defined in the future. The SWPP will keep the watch-list and be responsible for potential re-evaluations and post-use monitoring for surface water quality.

## 2. Methods and Materials

### 2.1 Overview

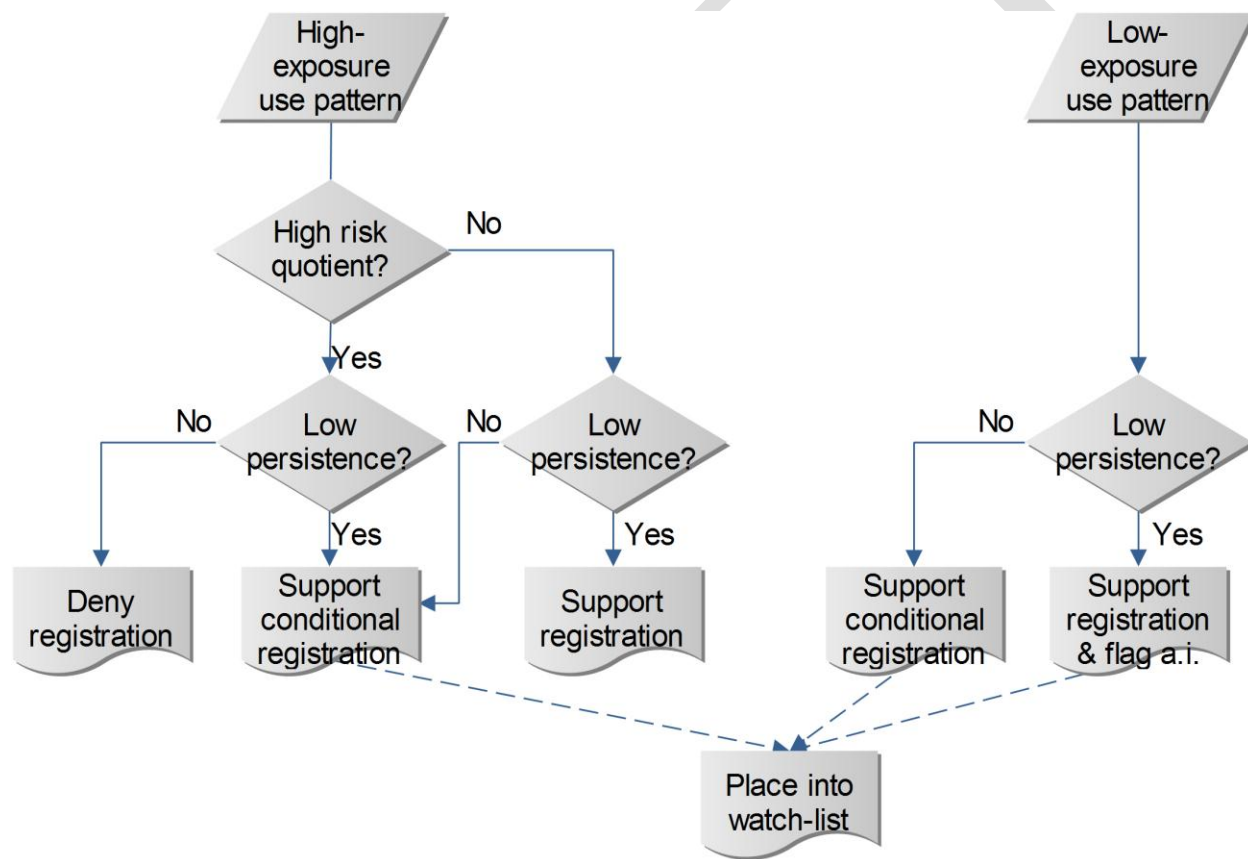


Figure 1. Decision flowchart for phase II evaluation based on refined modeling

The phase I evaluation identified pesticides which may potentially cause surface water problems. Additional evaluations are required for these pesticides based on the refined modeling approach described in this report as phase II evaluation. Figure 1 shows the flowchart for making registration recommendations and generating watch-list from the derived indicators. The indicators of use pattern, risk quotient (for high-exposure use pattern only), and aquatic

persistence are considered in the decision-making process. The indicator of persistence has been introduced in the companion report (Part I). The following sections provide detailed information on the development of the indicators of use pattern and risk quotient.

## **2.2 Pesticide Use Patterns**

Based on DPR's experience the following pesticide use patterns have high exposure potentials to surface water:

- 1) Aquatic pesticides
- 2) Rice pesticides
- 3) Urban pesticides
- 4) Pesticide applications to crops with gravity irrigation (Table 1)
- 5) Pesticide applications to crops with top acreages in California (Table 2)
- 6) Winter rain season applications
- 7) Pre-emergent applications

Crops in use pattern (4) "with gravity irrigation" are identified according to the results of a statewide survey of irrigation methods by crop in 2001 (CDWR, 2002). The survey of an estimated 80,000 growers requested information on the main county and acreages that were planted to each of 20 possible crop-categories by irrigation method in 2001 (Table 1). Gravity-based irrigation (flood and furrow) are considered to have high potentials for pesticide exposure because these are the least efficient from a water-use standpoint and have the greatest capacity to produce potential runoff to surface water. Crops with gravity-dominated (>50%) irrigation, as highlighted in Table 1, were selected as relatively high-exposure patterns of pesticide use. Here 50% is selected as an arbitrary value and assumed to provide protective criteria for the classification of pesticide use pattern according to dominant irrigation methods.

Table 1. Percent of crop acreage using specific type of irrigation in California statewide survey 2001.

Crop	Gravity			Sprinkler	Low volume	Subsurface
	Total	Flood	Furrow			
Corn	87.1%	19.1%	67.0%	0.8%	0.0%	12.1%
Cotton	93.9%	1.9%	86.4%	5.1%	0.0%	1.0%
Dry beans	56.9%	6.9%	37.2%	43.1%	0.0%	0.0%
Grains	87.3%	73.7%	12.7%	10.5%	0.0%	2.2%
Safflower	57.6%	27.4%	30.2%	27.8%	0.0%	14.6%
Sugarbeet	99.9%	0.0%	99.9%	0.0%	0.1%	0.0%
Other Field crops	85.1%	47.1%	38.0%	12.9%	1.7%	0.3%
Alfalfa	80.3%	71.9%	7.7%	17.4%	0.0%	2.2%
Pasture	75.1%	67.9%	2.7%	20.2%	0.0%	4.7%
Cucurbit	45.3%	3.3%	27.9%	23.6%	31.1%	0.0%
Onion & Garlic	43.7%	0.0%	14.9%	56.3%	0.1%	0.0%
Potato	1.2%	0.0%	1.2%	91.2%	7.6%	0.0%
Tomato (fresh)	61.3%	0.0%	27.0%	0.0%	38.7%	0.0%
Tomato (processing)	67.8%	0.0%	50.0%	30.2%	2.0%	0.0%
Other Truck Crops	36.1%	0.1%	16.0%	38.0%	25.9%	0.0%
Almond & Pistacio	19.2%	16.1%	0.6%	11.3%	69.3%	0.2%
Other Deciduous	33.7%	17.3%	16.2%	30.8%	35.0%	0.4%
Subtropical Trees	10.1%	3.8%	5.8%	12.5%	76.6%	0.9%
Turfgrass & landscape	0.6%	0.5%	0.1%	89.0%	10.2%	0.2%
Vineyard	20.8%	1.9%	18.8%	8.7%	70.2%	0.2%

Notes:

- 1) Crops with >50% gravity (flood and furrow) irrigation are highlighted
- 2) In addition to grain and pasture, field crops mainly includes corn, cotton, sugar beets, and dry beans, according to California Field Crop Reviews (USDA, 2011)

Crops in the use pattern (5) “with top CA acreages” are identified based on the Pesticide Use report (PUR) database (CDPR, 2011) and land use survey results (CDWR, 2011). In summary, citrus, deciduous fruits and nuts, field crops, grapes, rice, pasture, and tomatoes are considered to have high exposure potentials to surface water according to their acreages (Table 2).

Table 2. Top ten crops by acreage based on PUR database and DWR land use survey

By accumulated treated acreage		By land use data	
PUR site code	Crop	DWR land use code	Crop
3001	almond	P1	alfalfa
29141	grapes	F1	cotton
3011	pistachio	G**	grain
2000	citrus	V**	vineyards
43026	dried fruits	D12	almonds
3009	walnut	F6	corn
2006	orange	P3	mixed pasture
5004	peach	R**	rice
5005	plum	T15	tomatoes
29143	grapes, wine	F**	field crops

Note: Accumulated treated acreage is the summation of “acre\_treated” from multiple applications of all applied pesticides by “site\_code”, based on 2006-2010 PUR data;

## 2.3 Pesticide Risk Quotient

### 2.3.1 Risk Characterization

Estimation of risk quotient (RQ) is required for pesticides associated with high-exposure use patterns. Risk characterization integrates exposure and ecological effects to determine the potential ecological risk from the use of pesticides. The exposure and toxicity effects data are integrated in order to evaluate the risks of ecological effects on non-target species. For the assessment of pesticide risks, the risk quotient method is used to compare exposure and measured toxicity values. RQ is defined as estimated environmental concentration (EEC) divided by the acute toxicity value of the most sensitive aquatic organism (LC50, as defined in the report Part I):

$$RQ = \frac{EEC}{LC50} \quad (1)$$

The resulting RQs are then compared to the levels of concern (LOCs) suggested by USEPA. LOC of 0.5 was used in this project, when exceeded for acute risk to non-target organisms “may warrant regulatory action in addition to restricted use classification” (USEPA, 2004). If the RQ exceeds LOC, the corresponding pesticide product was marked as one with “high” risk quotient, indicating that the pesticide’s use, as directed on the label, has the potential to cause direct or indirect effects to non-target organisms. Otherwise, the product was designed to have a “low” risk quotient.

The estimations of EEC and RQ are mainly based on the use-exposure relationships developed in this study (in the Appendix). In addition, USEPA Tier 1 Rice Model is improved (see Section 2.3.2 Rice Pesticides) for estimating the risk quotient of rice pesticides. For other use patterns, such as general aquatic pesticides, which are not supported by any existing regulatory models, a protective assumption is applied by simply assigning a high risk quotient (Table 3).

Table 3. Approaches in determining risk quotients (RQ) for high-exposure patterns of pesticide use

Use pattern	Approach
Rice pesticides	RQ is calculated by modified USEPA Tier 1 Rice Model (Section 2.3.2)
Patterns covered by USEPA Tier 2 modeling scenarios	RQ is calculated by use-exposure relationships (Section 2.3.3 and the Appendix)
Patterns without model supports	A high RQ is assumed

### 2.3.2 Rice Pesticides

For rice pesticides, EEC was estimated as the initial concentration of dissolve pesticide in a rice paddy based on the Tier 1 Rice Model developed by USEPA (USEPA, 2007b):

$$C_w(0) = \frac{m'_{ai}(0)}{1.05 \times 10^{-3} + 1.3 \times 10^{-6} \cdot KOC} \quad (2)$$

where  $C_w(0)$  is initial pesticide concentration in water ( $\mu\text{g/L}$ ),  $m'_{ai}(0)$  is the mass applied per unit area ( $\text{kg/ha}$ ) and  $KOC$  is the organic carbon (OC)-normalized soil sorption coefficient ( $\text{L/kg[OC]}$ ). In the USEPA Tier 1 Rice Model, the water column depth was assumed to be 0.10 m. This value is lower than the representative depth of 0.127 m (or 5 inch) in California (CRC, 2010), thus generating a conservative estimation of the initial concentration. Pesticide equilibrium was assumed to be established between the dissolved and particulate phases. Therefore, the concentration of pesticide in suspended sediment ( $C_d$ ,  $\text{ng/g}$ ) was calculated based on  $KOC$  and OC content of sediment ( $f_{oc}$ , dimensionless):

$$C_d = C_w \cdot KOC \cdot f_{oc} \quad (3)$$

The Tier I Rice Model does not consider dissipation processes in either water column and bed sediment. In this study, concentration dynamics are estimated based on first-order degradation kinetics for pesticide decay during the water-holding period:

$$C_w(t) = C_w(0) \cdot \exp(-kt) \quad (4)$$

where  $t$  (day) is the required water-holding period, and  $k$  ( $\text{day}^{-1}$ ) is an overall rate constant of pesticide dissipation in the water-sediment system. Value of  $k$  could be conservatively set as the minimum value of the rate constants of pesticide dissipation in water column ( $k_w$ ,  $\text{day}^{-1}$ ) and in sediment ( $k_{sed}$ ,  $\text{day}^{-1}$ ). It can be also refined based on chemical properties and environmental parameters:

$$k = \frac{d_w k_w + d_{sed} (\theta_{sed} + KOC \cdot f_{oc} \rho_b) k_{sed}}{d_w + d_{sed} (\theta_{sed} + KOC \cdot f_{oc} \rho_b)} \quad (5)$$

Values of  $d_w$  (water depth),  $d_{sed}$  (sediment layer depth),  $\theta_{sed}$  (sediment porosity),  $\rho_b$  (sediment bulk density) and  $f_{oc}$  could be taken from the USEPA suggested values (USEPA, 2007b). Once  $C_w(t)$  is determined, the corresponding concentration in sediment could be calculated by Eq. (3).

### 2.3.3 Use Patterns Covered by USEPA Tier 2 Modeling Scenarios

The USEPA Tier 2 modeling scenarios developed for California (USEPA, 2006, 2008, 2010) cover most of the representative crop types and surface conditions in the identified high-exposure use patterns in this study: citrus, field crops (cotton and sugar beet as surrogates), grains (wheat), pasture (alfalfa), tomato, grapes, rainfall-season application (almond), pre-emergence application (turf), and hard surface (residential and right-of-way applications), as summarized in the Appendix.

USEPA regulatory model, Pesticide Root-Zone Model (PRZM), is selected for the determination of risk quotients based on the above modeling scenarios. To simplify the PRZM modeling processes, a meta-modeling approach with regression equations, called use-exposure relationships (Luo *et al.*, 2011), were developed based on results of stochastic PRZM simulations with 30-year meteorological data compiled by USEPA (USEPA, 2007c) at the stations specified in the modeling scenarios. EEC was defined as an average edge-of-field concentration over a given recurrence interval, also called exposure index (EI). For dissolved pesticides, EI was calculated as the maximum 4-day moving average concentration in a 3-year return period. This definition is consistent with the water quality criteria for chlorpyrifos and diazinon by USEPA and California Department of Fish and Game (CDFG) (Siepmann and Finlayson, 2000; USEPA, 2005), and with the 96-hour duration commonly used in acute aquatic toxicity test. For sediment-bound pesticides, there are no surface water quality criteria at either federal or state level at present. Water quality assessments for pesticides in sediment, such as those for Clean Water Act Section 303(d) listing (CEPA, 2010), are usually based on 10-day *Hyaella azteca* sediment toxicity tests (USEPA, 1999). To mimic the sediment toxicity tests, 10-day averages were calculated as adsorbed EI from PRZM-predicted daily concentrations of pesticide associated with soil erosion. The same frequency as for dissolved pesticide, i.e., once every three years return period, was used for adsorbed pesticides.

In the developed use-exposure relationships, the exposure index is a function of label rate and chemical properties:

$$EI = \frac{RATE}{BASE} \cdot EI\_BASE \quad (6)$$

$$\ln(EI\_BASE) = b_1 + b_2 \ln(AERO) + b_3 \ln(KOC) \quad (7)$$

where BASE (kg/ha) is a small application rate (set as 0.1 kg/ha) used to normalize the field runoff potentials of various label rates, RATE (kg/ha) is the actual application rate, EI\_BASE ( $\mu\text{g/L}$  for dissolved phase, and  $\text{ng/g}$  for adsorbed phase) is the exposure index from pesticide application at BASE rate, and AERO (day) is the aerobic soil metabolism half-life. The regression coefficients  $b$ 's in the equation are determined for a variety of crop types and surface conditions using USEPA recommended crop scenarios for California (USEPA, 2008) and provided in the Appendix. The parameterized relationships accounted for 90-95% of the

variances in the PRZM-predicted EI of dissolved pesticides for a 30-year period. For pesticide associated with eroded soil, the coefficients of determination ranged from 61% to 85%. The resulting RQ value will be used in the place of EEC of Eq. (1) to calculate the corresponding risk quotient.

## **2.4 Pesticide Watch-list Requirements**

### **2.4.1 Requesting Analytical Methods**

In California, both DPR and the State and Regional Water Boards have mandates and authorities regarding pesticides and water quality. DPR's mandates include ensuring that all pesticides registered in California are used in a manner that protects the environment. The Water Boards administer multiple regulatory programs in both agricultural and urban areas that require environmental monitoring to assess the impacts of pesticides in surface water (CDPR, 2001).

Core to all water quality regulatory programs is the need to conduct surface water and sediment monitoring to characterize pesticides in water bodies in order to assess potential environmental impacts. In order to conduct pesticide residue monitoring, regulatory agencies need to have access to chemical analytical methods. Currently, analytical methods sensitive enough for detecting pesticide residues at levels that can cause toxicity to aquatic organisms are available for only a small fraction of registered pesticide active ingredients.

Before a pesticide is registered for use in California, DPR evaluates it to determine that it can be used without significant adverse effects to human health or the environment. The law requires prospective registrants to conduct and submit to DPR various tests and data on new pesticide products for this evaluation (CDPR, 2001). While registrants are required to submit analytical methods for commodity residue during the registration process; they are not currently required to provide the more sensitive analytical methods suitable for the analysis of residues in water or sediment at environmentally relevant concentrations. Thus, surface water quality monitoring programs for new pesticides cannot begin without first developing more sensitive analytical methods with sufficiently low detection levels.

As a condition of full registration Surface Water staff requests the registrant to develop analytical methods for the active ingredient and relevant degradation products for detection in water and in sediment. The analytical methods should meet the following specifications:

1. The methods should be routinely executable by commercial laboratories. Reporting limits (RL) are set at 3 - 5 times method detection limits (MDL), and RLs should be no greater than  $0.05 \mu\text{g L}^{-1}$  [water] and  $1 \mu\text{g kg}^{-1}$  [sediment]. A need for a lower RL may be necessary based on aquatic toxicity data. If so, the RL needed will be identified in the evaluation report. Method detection limits are determined as described in 40 CFR Ch.1, part 136 appendix B, "Definition and procedure for the determination of the method detection limit" (Segawa, 1995).
2. The method should be gas chromatography (GC) or high pressure liquid chromatography (HPLC)-based methods with mass spectral (MS) detection preferred. Other methods (e.g.



HPLC with fluorescence detection; GC with thermionic specific detection) may be used with justification, but the MS-based detection is strongly preferred due to specificity.

3. Analytical method documentation shall include all method validation data. Method validation shall be conducted as described in DPR's "Chemistry Laboratory Quality Control: standard operating procedure (Segawa, 1995). Briefly, water methods shall include triplicate analysis at each of six concentration levels: 0 (blank spike), 0.025, 0.05, 0.1, 0.2 and 1  $\mu\text{g L}^{-1}$ . Soil or sediment methods shall include triplicate analysis at each of six concentration levels: 0 (blank spike), 0.1, 0.2, 0.5, 2 and 10  $\mu\text{g kg}^{-1}$ .
4. Acceptable overall mean method validation recoveries are  $70\% < \text{recovery} < 120\%$  with relative standard deviation (RSD) of  $<20\%$ .
5. A minimum 30-day sample storage stability study will be required in the respective matrix, water and/or sediment.

#### **2.4.2 Flagging the A.I. for re-evaluation with label changes**

Some pesticides may pass the phase II evaluation and be supported for registration mainly because the products under evaluation are associated with low-exposure use patterns. The active ingredients may potentially cause surface water problems (otherwise they won't be required for additional evaluations in phase II), especially under high-exposure use patterns. Therefore, these active ingredients are placed into the watch-list and should be flagged for re-evaluation if a new label comes with high-exposure use patterns.

### **3. Methodology Testing**

The developed procedure for pesticide evaluation was tested with the pesticide products recently evaluated by the SWPP. Selected pesticides with their physiochemical properties and toxicity data were described in the report Part I. Indicators for aquatic persistence was also derived in Part I. In this test, detailed information on use pattern and use rate was retrieved from their labels (Table 4) for developing respective indicators. Results of the model-based evaluation (Table 5) were compared to results of best professional judgment from the evaluation reports. The purpose of the test is to demonstrate the validity and consistency of the proposed evaluation procedure and its capability for assessing pesticides for registration in California.

Table 4. Use patterns and use rates (kg/ha) for selected pesticides

Active ingredient	Product	Use pattern (1)	Max. use rate (2)
A	A1	mosquito or midge control	
B	B1	pre-emergence herbicide	0.1
		residential turf	0.1
	B2	stone fruits, tree nuts	0.1
	B3	residential turf	0.1
C	C1	sugar beet	0.81
D	D1	field corn	0.07
E	E1	soybean and apples	0.65
F	F1	mosquito adulticide	
G	G1	anti-fouling preservative	
H	H1	residential turf	2.24
	H2	peanuts, stone fruits, tree nuts	0.56
	H3	sugar beet	0.04
I	I1	rice	1.12
J	J1	grapes	0.09
	J2	sugar beet	0.21
K	K1	burndown herbicide	
L	L1	wheat	0.06
M	M1	greenhouse and Nursery	
N	N1	vegetables, grapes, sweet potato	0.33
O	O1	greenhouse	
P	P1	cereals, cotton, corn, sugar beet, vegetable, potato	0.52
Q	Q1	tomato	0.22
	Q2	turf, ornamentals, interior landscapes, and sod farms	
R	R1	rice	0.35
S	S1	rice	0.31
T	T1	grapes	2.02
U	U1	residential turf	1.50

Notes:

- 1) Only selected high-exposure patterns are tabulated and used in the demonstration.
- 2) Maximum use rates (kg/ha per year or per season) are only listed for modeled use patterns (Table 3).

Table 5. Registration recommendations from model-based evaluation vs. best professional judgment for surface water protection

Active ingredient	Recommendations by phase I evaluation (1, 2)		Product	Recommendations by phase II evaluation (3)		Best professional judgment based recommendations
	Dissolved phase	Adsorbed phase (4)		Dissolved phase	Adsorbed phase (4)	
A	S	S	A1			S
B	R	-	B1	C	-	S
				C	-	
			B2	C	-	
			B3	C	-	
C	R	R	C1	S	N	C (sed. toxicity test & runoff test)
D	S	-	D1			S
E	S	-	E1			S
F	S	S	F1			S
G	R	R	G1	C	C	C (marine test)
H	R	S	H1	S	S	C (sed. toxicity test)
			H2	S	S	
			H3	S	S	
I	R	S	I1	S	S	S
J	S	S	J1			C (sed. toxicity test)
			J2			
K	S	-	K1			S
L	S	-	L1			S
M	S	-	M1			S
N	R	-	N1	C	-	C (runoff test)
O	S	-	O1			S
P	R	S	P1	S	N	S
Q	R	-	Q1	C	-	C (runoff test)
			Q2	S	-	
R	R	S	R1	S	C	N
S	R	S	S1	S	S	S
T	S	S	T1			S
U	S	-	U1			S

Notes:

- 1) “S” = Support registration without conditions; “N” = not to support registration; “C” = support conditional registration; and “R” = require additional evaluation (for the results of phase I evaluation only). “Best professional judgment based recommendation” was the original recommendations in the evaluation reports.

- 2) Results of phase I evaluation are taken from the report Part I.
- 3) Shaded cells in phase II evaluation: the corresponding pesticide has been classified in the phase I evaluation as “unlikely to be a surface water problem” and registration is supported with no condition, thus phase II evaluation is not required.
- 4) Evaluation for sediment-bound pesticides was only conducted for those with KOC > 1000, for which USEPA requires sediment toxicity tests (USEPA, 2007a). For pesticides without reported sediment toxicity, we estimated sediment toxicity from the corresponding water toxicity. Therefore, the evaluation results for adsorbed pesticides won’t be used in the comparisons best professional judgment based recommendations. Details in the estimation were documented in Part I report.

The performance of the phase II evaluation was validated by comparing the recommendations for dissolved pesticides from the refined modeling and from best professional judgment. Generally, the proposed evaluation procedure generated comparable results as those by best professional judgment based on the following criteria (Table 6).

Table 6. Criteria used in the comparison of model-based and professional judgment based decisions in the methodology testing

Model-based decisions (for dissolved phase)	...is considered to be comparable to ...	Best professional judgment based decisions
Support registration [S]	→	Support registration [S]
Support registration [S]	→	Support conditional registration with only request of sediment toxicity test [C (sed. toxicity test)]
Support conditional registration [C]	→	Support conditional registration with request of runoff test [C (runoff test)]

Different recommendations were generated for 3 out of the 21 tested active ingredients compared to the decisions from best professional judgment. Detailed investigations are provided for these pesticides (B, C, and R) as follows:

1. The SWPP reviewed several registration data packets for products containing the new active ingredient B in May 2010, and recommended that the products be conditionally registered due to potential impacts to surface water quality. The registrant provided additional information in response to DPR’s registration decision. SWPP staff re-reviewed the submitted data in December 2010 and concluded that “while there is still cause for concern over potential off-site movement of this pesticide, an edge-of-runoff study is not necessary”.
2. The best professional judgment for C with decision to request additional information on environmental concentrations in surface water was mainly based on the potential accumulation in sediment. The model-based results indicated that its rapid degradation in water and low RQ value would result in low concern for risk to aquatic species in water column.
3. For R, best professional judgment did not support its registration because the calculated “conservative maximum concentration is comparable to the lower-end acute toxicity benchmarks”. Results of the phase II evaluation indicated that the resulting RQ was less

than LOC of 0.5, thus the labeled use rate was not likely to cause adverse effects in water column of receiving water bodies.

Based on the results of methodology testing (Table 5), the following active ingredients should be placed into the watch-list: B, G, N, and Q with request of analytical methods and potential post-use monitoring. No active ingredients in the test are required to be flagged for re-evaluation with label changes.

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## Appendix: Determination of Risk Quotients Based on Tier 2 Modeling Approach

This appendix provides detailed information for model development and applications for the determination of pesticide risk quotients associated with high-exposure use patterns. Modeling development has been published as a separate paper, Luo, Y., F. Spurlock, X. Deng, S. Gill, and K. Goh, 2011. *Use-Exposure Relationships of Pesticides for Aquatic Risk Assessment*, PLoS ONE, 6(4): e18234 (<http://dx.plos.org/10.1371/journal.pone.0018234>). This paper also reported derived model parameters for almonds, field crops, pasture, and tomatoes.

### Supplementary material #1: Summary of Modeling Scenarios and Derived Parameters for Crops Representing High-Exposure Use Patterns of Pesticides

Table 7. USEPA tier 2 crop scenarios for California: (a) overview and (b) landscape characteristics

(a)

Crop scenario	Represented use pattern	Soil (hydrologic group)	Weather station
Alfalfa (OP)	Pasture, gravity irrigation	Sacramento clay (D)	Fresno
Almond (STD)	Dormant application	Manteca fine sandy loam (C)	Sacramento
Citrus (STD)	Citrus, top CA acreage	Exeter loam (C)	Bakersfield
Cotton (STD)	Field crop, gravity irrigation	Twisselman Clay (C)	Fresno
Grapes (STD)	Grapes, top CA acreage	San Joaquin loam (C)	Bakersfield
Sugar beet (OP)	Field crop, gravity irrigation	Ryde clay loam (C)	Fresno
Tomato (STD)	Tomato, gravity irrigation	Stockton clay (D)	Fresno
Turf (RLF)	Pre-emergent application	Capay Silty Clay Loam (D)	San Francisco
Wheat (RLF)	Grain, gravity irrigation	San Joaquin Loam (D)	Fresno

(b)

Crop scenario	CN	USLE K/LS/P	USLE C	OC1
Alfalfa	90/88/89	0.20/0.30/1.0	0.051-0.217	1.77%
Almond	84/79/84	0.28/0.30/1.0	0.034-0.221	0.81%
Citrus	84/79/82	0.28/0.21/1.0	0.096-0.150	0.46%
Cotton	89/86/89	0.21/0.37/1.0	0.054-0.412	0.29%
Grapes	84/79/82	0.28/0.2/1.0	0.274-0.517	0.72%
Sugar beet	89/86/89	0.28/0.30/1.0	0.015-0.769	3.48%
Tomato	91/87/91	0.24/0.13/1.0	0.035-0.255	0.95%
Turf	80/80/80	0.37/1.80/0.5	0.001	35.6%
Wheat	92/89/90	0.37/0.79/1.0	0.027-0.604	0.44%

Data source:

USEPA Tier 2 crop scenarios for PRZM/EXAMS Shell (USEPA, 2006, 2008, 2010). “STD” = Standard crop scenarios, “OP” = scenarios developed for the cumulative risk assessment of

organophosphate pesticides, and “RLF” = scenarios developed for the effects determinations for the California red-legged frog and other California listed species.

Parameters:

CN = Runoff curve numbers of antecedent moisture condition II for fallow, cropping, and residue, respectively;

USLE K = soil erodibility for the universal soil loss equation (USLE);

USLE LS = topographic factor for the USLE;

USLE P = practice factor for the USLE;

USLE C = cover management factor for the USLE;

OC1 = Organic carbon content in the surface soil.

Table 8. Use-exposure relationships for (a) dissolved pesticides and (b) sediment-bound pesticides in selected California crop scenarios

(a)					
Scenarios	Coefficients			R <sup>2</sup>	lnKOC*
	b1	b2	b3		
Alfalfa	5.2156	0.1907	-0.8288	0.9494	3.5
Almond	4.8131	0.1869	-0.7467	0.9335	4.5
Citrus	6.6724	0.1597	-0.7952	0.9161	5.0
Cotton	6.3173	0.1467	-0.7662	0.9102	5.5
Grapes	6.5127	0.1694	-0.8081	0.9286	4.5
Sugar beet	4.9105	0.2412	-0.8377	0.9193	3.0
Tomato	5.9979	0.1785	-0.7844	0.8970	4.0
Turf	3.3647	0.2821	-0.8248	0.9546	0.5
Wheat	6.0764	0.1853	-0.7954	0.9487	5.0

(b)					
Scenarios	Coefficients			R <sup>2</sup>	ln(KOC*)
	b1	b2	b3		
Alfalfa	1.7756	0.3140	0.4936	0.6896	9.5
Almond	0.1179	0.2116	0.6937	0.7955	10.0
Citrus	3.4796	0.2098	0.6346	0.8189	10.5
Cotton	0.9213	0.1890	0.7221	0.8466	11.0
Grapes	3.0443	0.2376	0.5991	0.7780	10.0
Sugar beet	2.7386	0.3254	0.5118	0.6409	8.5
Tomato	3.2070	0.1912	0.6062	0.7770	10.0
Turf	2.7715	0.2832	0.4486	0.6106	6.5
Wheat	1.0782	0.3233	0.5848	0.7210	10.5



## Supplementary material #2: Development of Use-Exposure Relationship for Pesticide Applications to Impervious Surfaces

### S2.1 Scenarios for Impervious Surfaces

The USEPA impervious scenario for California was developed based on the environmental configurations in the San Francisco Area (USEPA, 2010). The impervious scenario was characterized by high curve numbers and zero surface OC content. PRZM accepts either KOC or the distribution coefficient (KD) as inputs for phase partitioning. When KOC is used, KD value will be automatically calculated by PRZM as the product of KOC and OC. In the previous scenarios, KOC is usually used to conveniently reflect the variation of soil OC content over various soil types. However, the KOC-based pesticide partitioning was not appropriate for impervious surfaces for which zero OC content is assumed for ground surface. Instead, the value of KD was used directly as input parameter in the PRZM runs. The exposure index from pesticide application at BASE rate for impervious surface was calculated based on the regression equation similar to (12).

$$\ln(EI_{imp\_BASE}) = f(AERO, KD) = b_1 + b_2 \ln(AERO) + b_3 \ln(KD) \quad (8)$$

For impervious surfaces, the AERO should be set as the field dissipation half-life in the corresponding surface conditions. It's assumed that KD followed the same distribution as KOC. Please note that this assumption was only used for generating random numbers for the stochastic simulation of PRZM. For a specific pesticide, its KD value for impervious surface should be taken from registrant-submitted chemical property data. Based on the regression analysis described in Appendix 2 for pervious surfaces, the use-exposure relationships were developed for impervious portions of residential and rights-of-way land use conditions in California (Table 9).

Table 9. Use-exposure relationships for dissolved pesticides in selected California scenarios for impervious surfaces

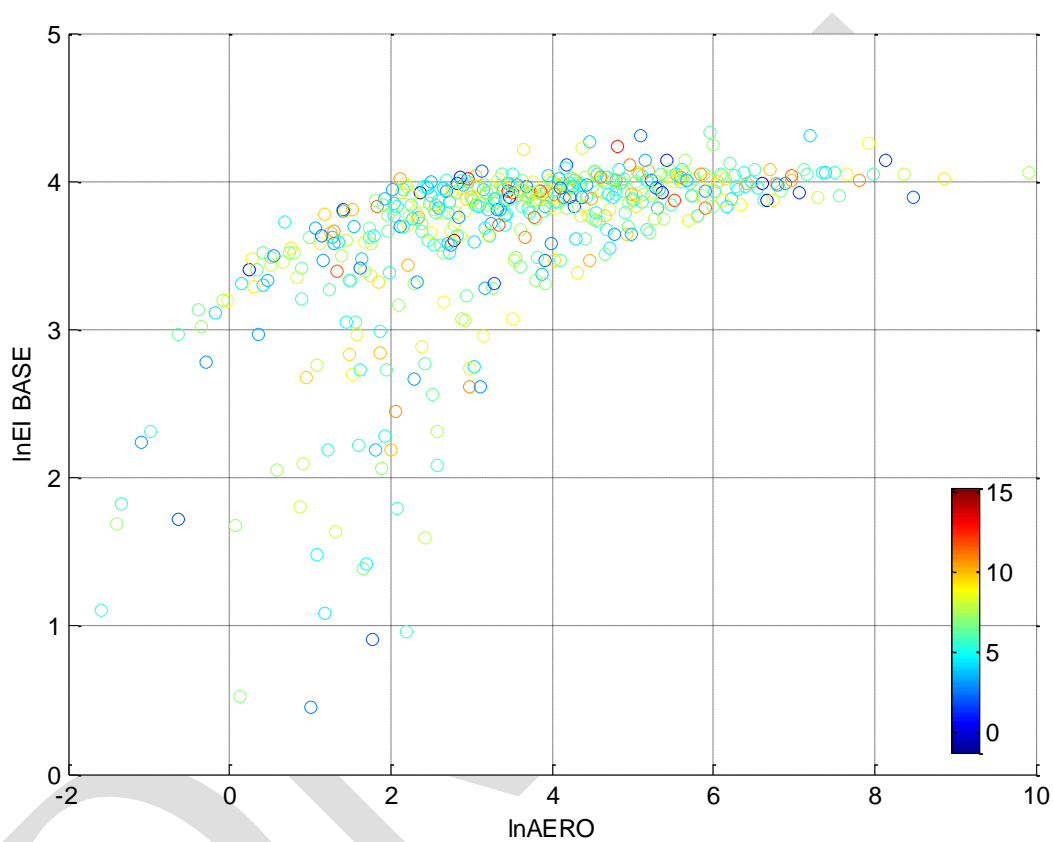
Scenarios	Coefficients			R <sup>2</sup>
	b1	b2	b3	
Residential [impervious]	1.1738	0.3880	-0.8814	0.8873
Rights-of-way [impervious]	1.9427	0.2831	-0.8667	0.9635

If KD value was not available for the evaluated pesticides, the conservative estimation could be conducted based on KD=0. The simulation results may overestimate the pesticide residues, but generate conservative predictions for pesticide exposure from application on impervious surfaces. The conservative estimation could provide useful information in screening processes of pesticide risk, especially for pesticides with high mobility and pesticides without actual KD values available for impervious surfaces. Monte Carlo simulation with 500 PRZM runs was conducted to characterize the effects of AERO on the conservative estimation of EI\_BASE (with KD=0) in impervious scenarios of California (Figure 2). Generally, lnEI\_BASE increased with AERO values and converged around 4.0 when lnAERO ≥ 2. Resulting lnEI\_BASE values did not

exceed 4.5 in both evaluated scenarios, suggesting a maximum EI\_BASE of 90 µg/L for pesticides with  $\ln AERO \geq 2$ . For pesticides with short soil half-life, a simple linear equation was applied to estimate the maximum EI\_BASE. The final equation was expressed as,

$$\ln EI\_BASE = 0.625 \cdot \min(\ln AERO, 2) + 3.25 \quad (9)$$

[a]



[b]

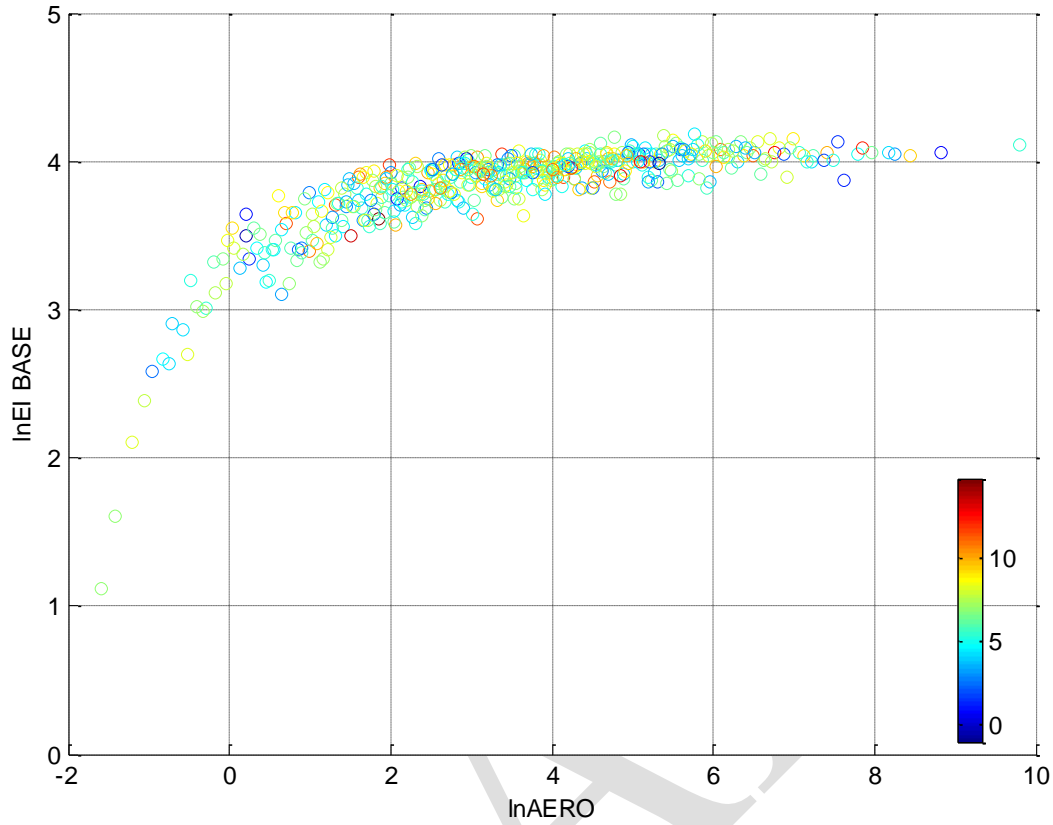


Figure 2. Conservative estimation (with KD=0) of EI\_BASE for dissolved pesticides from California impervious scenario of [a] residential and [b] right-of-way areas (Colorbars for lnKOC)

## S2.2 Post-Processing for Mixed Surfaces

Complex scenarios were developed by USEPA for pesticide application and overspray on residential and rights-of-way areas (USEPA, 2008). Those complex scenarios consist of paired pervious and impervious portions of land uses. The sub-scenarios for pervious and impervious surfaces were first simulated independently. The resulting daily EECs were added together based on the coverage fractions of the pervious and impervious surfaces defined in the scenarios. The coverage fraction of impervious surface ( $f_{imp}$ ) was set as 5.68% for residential area, and 1.00% for rights-of-way area. Details in the derivation of representative fraction of impervious surface were documented by USEPA (2010). Based on the linear assumption between pesticide use and exposure index, the overall exposure index (EI\_BASE) for the complex scenarios with impervious surfaces could be calculated as

$$EI\_BASE = (1 - f_{imp})EI\_p\_BASE + f_{imp}EI_{imp\_BASE} \quad (10)$$

where  $EI\_p\_BASE$  and  $EI_{imp\_BASE}$  are the exposure indices from pesticide application at BASE use rate generated from independent simulations of pervious and impervious surfaces,

respectively. The EI values for impervious surface were based on Eqs (8) and (9). The EI values from paired pervious surfaces were generated from USEPA scenarios for typical plants adjacent to residential and right-of-way areas (Table 10). It's noteworthy that, since soil erosion is disabled in the PRZM scenarios for impervious surfaces, pesticide exposure in adsorbed phase is only evaluated based on the pervious portion of the mixed surfaces.

Table 10. California scenarios for typical plants adjacent to residential and right-of-way areas (USEPA, 2010)

[a] Environmental configuration

Parameters	Residential [pervious]	Right-of-way [pervious]
Represented plants	Residential turf	European weeds, mustard, thistles, etc., in light density
Soil (hydrologic group)	Tierra Loam (D)	Gaviota sandy loam (D)
Weather station	San Francisco	Santa Maria
CN	83/83/83	92/92/92
USLE K/LS/P	0.32/0.37/1	0.28/1.1/1
USLE C	0.001	0.004
OC1	35.6%	0.44%

[b] Derived parameters

Scenarios	Coefficients			R <sup>2</sup>	ln(KOC*)
	b1	b2	b3		
<i>Dissolved phase:</i>					
Residential [pervious]	3.3054	0.2457	-0.8182	0.9554	0.5
Rights-of-way [pervious]	6.0914	0.2416	-0.7856	0.9330	5.0
<i>Adsorbed phase:</i>					
Residential [pervious]	0.7986	0.2911	0.6262	0.7693	6.5
Rights-of-way [pervious]	3.0013	0.2283	0.5177	0.8035	10.5

Notes:

CN= Runoff curve numbers of antecedent moisture condition for fallow, cropping, and residue, respectively;

USLE K = soil erodibility for the universal soil loss equation (USLE);

USLE LS = topographic factor for the USLE;

USLE P = practice factor for the USLE;

USLE C = cover management factor for the USLE;

OC1 = Organic carbon content in the surface soil.